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CHARGED PARTICLE REACTIONS OF IMPORTANCE IN THE IONOSPHERE

BY

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GODDARD SPACE FLIGHT CENTER
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**CHARGED PARTICLE REACTIONS OF IMPORTANCE
IN THE IONOSPHERE**

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**National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland**

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INTRODUCTION

Recent advances in measurements of the solar spectrum in the vacuum ultraviolet and X-ray regions have led to a better understanding of the process of photoionization of the terrestrial atmosphere. The number density and species of ions produced should in most instances be proportional to the relative concentrations of the neutral gases comprising the atmosphere, but the final result will depend on the lifetime of an electron-ion pair and interactions between ions and neutral particles.

In fact observational results of the ionosphere cannot be explained without invoking varying ion-electron recombination rates for different species of ion and ion-neutral reactions. Figure 1 is a description of the daytime ionosphere. Representative electron densities are given for the various ionospheric layers together with the radiations thought to be responsible. The primary ions produced at various heights by photoionization are indicated with secondary ions given in parentheses. In the lowest part of the ionosphere negative ions are formed by attachment of free electrons to various molecules.

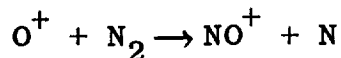
An analysis of ion composition obtained by means of rocket-borne mass spectrometers is shown in Figure 2. NO^+ , an ion which is not produced in any quantity by photoionization, plays a prominent role, while O_2^+ appears in varying amounts depending on ionospheric conditions. A comparison of the noon with the night profile indicates that after sunset the percentage of O_2^+ at 100 km decreases while NO^+ remains up to 200 km. Above that altitude O^+ is the predominant ions. The Fort Churchill data were

taken during disturbed conditions and this may account for the increased proportion of O_2^+ at 100 km compared to the Wallops Island experiment.

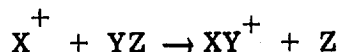
Since these results and others cannot be explained by simple ion-electron recombination, it is necessary to consider ion-neutral reactions. The purpose of this memo is to list those reactions which are considered to play a prominent role in the ionosphere and whose rate coefficients are in most urgent need of study in order to obtain a quantitative model of the ionosphere.

ION-ATOM INTERCHANGE

The existence of NO^+ above 100 km can best be explained by the reaction

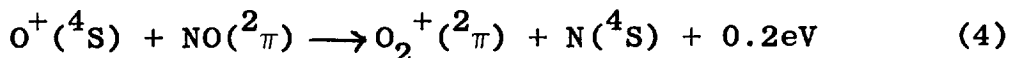
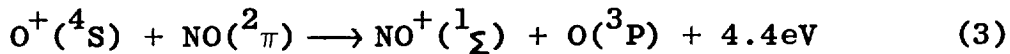
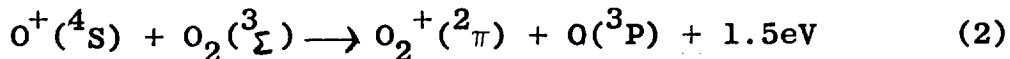
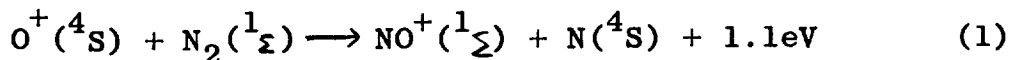


This is an example of an ion-atom interchange process and is analogous to the chemical reaction

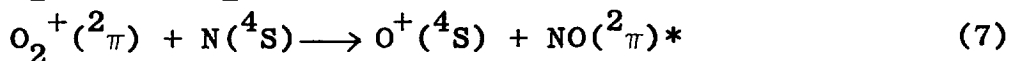
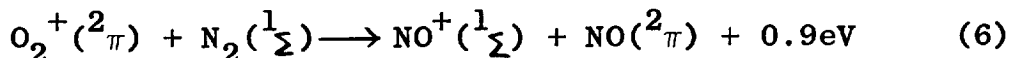
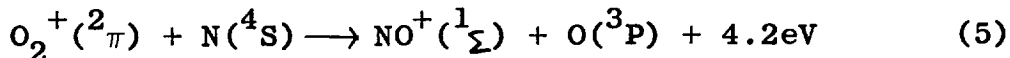


Many other reactions of this type can occur in the ionosphere and in fact other ions beside O^+ can be involved. Bates & Nicolet (1960) and Nicolet (1961) have listed the following exothermic reactions as being of importance in the ionosphere.

Those involving the atomic oxygen ion are:

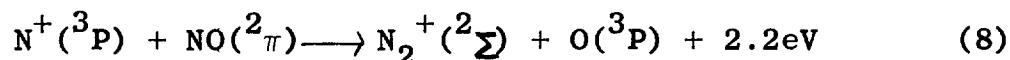


The reactions for O_2^+ are:

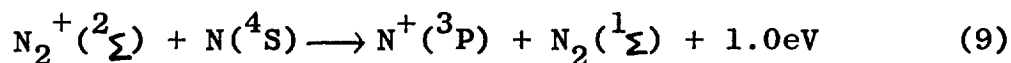


* This reaction is important only for temperatures above 500°K where the number of $\text{O}_2^+(^2\pi)$ with $v \leq 1$ is equal to or greater than $5 \times 10^{-3}n(\text{O}_2^+)$ in the normal state.

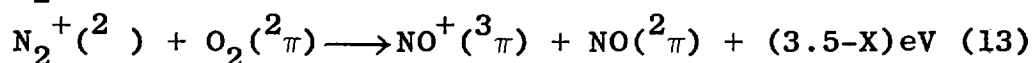
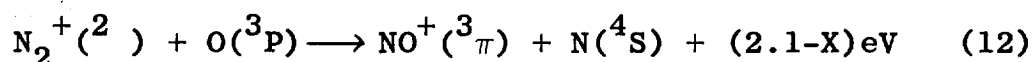
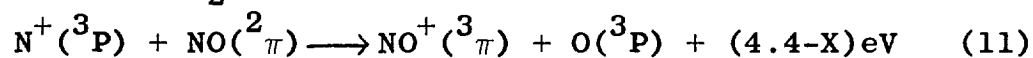
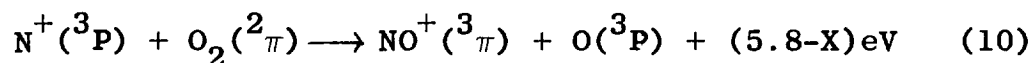
Atomic nitrogen ions take part in the reaction



while molecular nitrogen ions can react with atomic nitrogen through



Nitrogen ions can also form NO^+ by means of the reactions



In the case of reactions (10) through (13) NO^+ is formed in an excited state. X denotes the excitation energy needed to form NO^+ from N^+ and O. This energy may be enough to render these reactions endothermic and they would probably not play a very important role in the ionosphere except where the number density of the reactants is quite large.

By means of simple collision theory, the rate coefficient for these processes can be written as

$$k = Pz \exp \left[- E_o/RT \right]$$

z represents the collision number which, based on the assumption of an attractive polarization force between ion and neutral particle, varies between 10^{-9} and $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ for the reactions given above. The exponential factor shows the effect of E_o , the activation energy, which will always be greater than zero. E_o is the quantity with the greatest uncertainty in the determination of rate coefficients for

ion-atom interchange processes involving nitrogen and oxygen. The deviation of the reaction rate from that expected on the basis of simple collision theory is represented by P the steric hindrance factor. The utilization of statistical mechanics yields a value of this quantity ranging from unity to 10^{-2} for ion-neutral particle reactions.

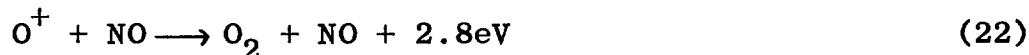
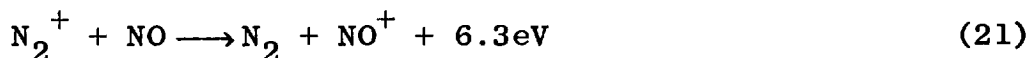
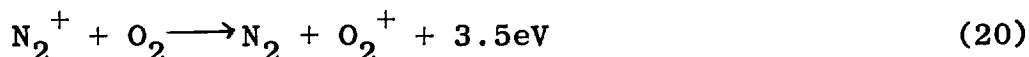
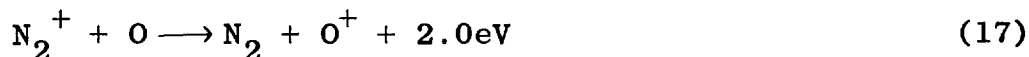
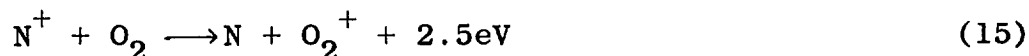
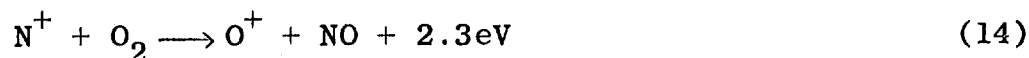
On this basis one would expect the rate coefficients for oxygen-nitrogen systems to have an upper limit of $10^{-9} \text{ cm}^3 \text{ sec}^{-1}$. Of the reactions listed only the rate coefficient of (2) has been measured with any precision. Dickinson and Sayers (1960) give a value of $2.5 \pm 0.4 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ in the temperature range 200-300°K. Utilizing ionospheric recombination rates and ion composition, Bates and Nicolet (1961) give

$$k_1 + 0.16 k_2 = 1.3 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$$

for temperatures of 1000°K. An analysis of Figure 2 by Harteck and Reeves (1961) led to the conclusion that the upper limits for the reaction rates of (1), (2) and (6) were 10^{-13} , 10^{-12} and $10^{-14} \text{ cm}^3/\text{sec}$ respectively.

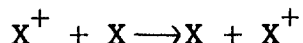
CHARGE EXCHANGE

Several processes involving charge exchange are of importance when the energy of the particles is high enough. However, it has been pointed out by Bates (1955) that except where resonance is involved the rates at thermal energies of this type of reaction are lower than ion-atom interchange. One might, therefore, expect a value of $10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ or less for the rate of reactions which involve only the transfer of an electron. No measurement has been made at thermal energies and the following reactions should be considered.



These reactions should be less important than reactions (1) to (13) but an analysis should be made at low energies to determine the exact rate coefficients.

Reactions involving a symmetric transfer of charge such as



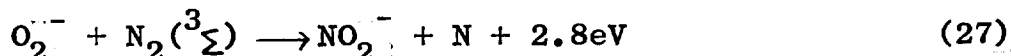
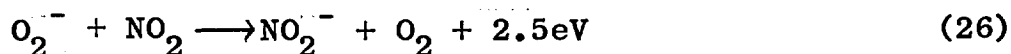
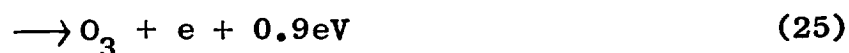
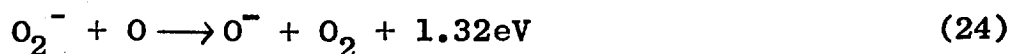
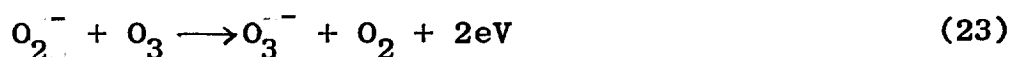
are more rapid at thermal energies than those listed above. However, they must be considered only from the standpoint of their effect on the mobility of ions in their parent gases. This will have particular importance in conductivity measurements and in the determination of the distribution of charged particles at high altitudes.

NEGATIVE IONS

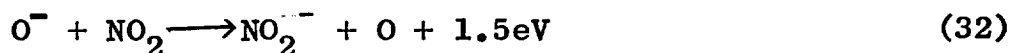
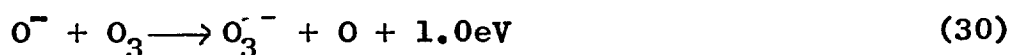
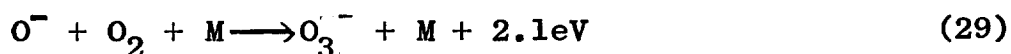
In the lowest part of the ionosphere, that is below 70 km, negative ion densities are considered to be comparable to or greater than electron densities. Utilizing experimental results of photodetachment cross-sections and attachment processes Nicolet and Aikin (1960) have demonstrated

that O_2^- is the principal negative ion in the ionosphere with O^- contributing a negligible addition to the total density. A recent measurement by Van Lint (private communication to Haaland 1961) has indicated that the three-body attachment process of electrons to NO_2 is 10^3 times greater than the corresponding process for O_2 . However, since $n(NO_2) = 10^{-13} n(O_2)$ the number of NO_2^- formed in this manner is negligible. Attachment of electrons to O_3 is also a very rapid process, but the number density is $5 \times 10^{-6} n(O_2)$ at 60 km. Thus O_2^- is the principal negative ion unless processes are operative between negative ions and neutral particles.

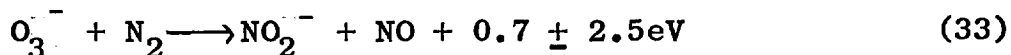
The following reactions are possible for O_2^- .



O^- may enter through the reactions



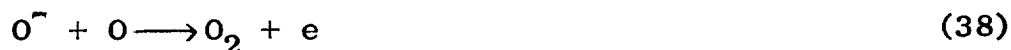
The negative ion of ozone may react through



The rate coefficients are unknown for most of these reactions. Bates and Massey (1952) have estimated that (25) may have a rate of $5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$. By analogy with three-body chemical reactions (29) may be $10^{-28 \pm 2}$. A measurement of $4 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ has been reported by Hinglein and Muccini (1959) for (32). In addition (28) results in an excited state of O_2^- for which the lifetime is not known. Also (27) involves an excited state of N_2 .

The remaining reactions are mainly charge exchange. One might expect that their rates were of the same order of magnitude as (32). Haaland (1961) has assumed a value of $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ for this set of reactions. With coefficients this large a calculation leads to NO_2^- as the principal negative ion of the D region.

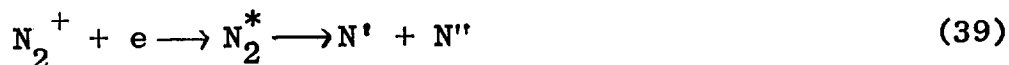
An analysis of ionospheric polar cap absorption events has been carried out by Whitten and Poppoff (1962). In addition to (24) and (25) the following processes may be important to give an effective associative detachment coefficient for negative ions in the D region.



A coefficient which may be as large as $10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ is derived from the ionosphere data.

DISSOCIATIVE RECOMBINATION

There are three reactions of this type which determine the lifetime of an electron-ion pair in the ionosphere. The first two involve N_2^+ and O_2^+ through



and



Although N_2^+ is produced in sufficient quantity to be an important ionospheric ion, its presence has not been detected. This would seem to indicate that either the rate of dissociative recombination is large compared to the same process for other ions or the N_2^+ is involved in ion-atom interchange or charge exchange reactions. Many attempts have been made to measure the rate of this reaction. Most recently Kasner, Rogers and Biondi (1961) have indicated the need for mass spectrographic identification of ions and the use of pressures approximating the partial pressures of nitrogen found in the atmosphere above 75 km, no greater than 0.01 mm Hg. For higher pressures N_3^+ and N_4^+ ions were formed. A similar analysis holds for reaction (40). The measured rate coefficients for (39) and (40) were 6×10^{-7} and 4×10^{-7} cm^3/sec respectively.

Since the end product of most of the ionospheric processes is NO^+ , there is great need to study the reaction



A value of 10^{-6} cm^3/sec was obtained by Gunton and Inn (1961) at a pressure of a few tenths of a millimeter but no ion identification technique was utilized. A

recombination rate of $10^{-6} \text{ cm}^3/\text{sec}$ is unacceptable to ionospheric workers since it would lead to a rapid disappearance of this ion. Nicolet and Aikin (1960) have suggested $3 \times 10^{-9} \text{ cm}^3/\text{sec}$ for temperature of 200°K but it may be as high as $3 \times 10^{-8} \text{ cm}^3/\text{sec}$.

A theoretical calculation by Squires (1961) for electrons of energy 1 eV recombining with NO^+ given a cross-section of $12 \times 10^{-16} \text{ cm}^2$. This is four times the value assumed by Nicolet and Aikin at 0.04 eV. It is suggested that if any research is performed in this area that it be carried out on the $\text{NO}^+ - \text{e}$ system. Furthermore, the ion identification techniques of Biondi should be utilized, the experiment being carried out at pressures and temperatures comparable to those prevailing in the ionosphere.

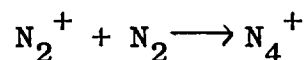
CONCLUSIONS

The reactions discussed here are felt to be those important in the ionosphere. There is urgent need of study of systems involving (O^+ , O_2 , N_2 , NO). Atomic nitrogen ions play some role in determining the charged particle environment, and they are produced in the upper part of the ionosphere by radiations of wavelength less than 500 \AA . The importance of charge exchange vs. ion-atom interchange must be determined. For the case of ion-atom interchange the rate coefficient will be mostly influenced by the activation energy of the reaction. If this energy is negligible then rate coefficients as high as $10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ will predominate. Hertzberg (1961) has shown that if values of this order are used the atomic nitrogen concentration will differ substantially from that determined by the dissociative recombination of N_2^+ .

Charge exchange may be an important process in determining the species of negative ion to be found in the D region. It would be worthwhile to perform some experiments involving (O_2^- , NO_2 , O, O_3) and (O^- , O_2 , O_3 , NO_2). Also, reactions in which charge exchange occurs between O_2^- and NO might be important.

The presence of He^+ and H^+ in the upper ionosphere as well as neutral helium, atomic oxygen, and molecular nitrogen may imply that reactions occur between these and other particles. Processes involving these constituents should be investigated.

In a summary of their recently completed experimental investigations Rutherford, Fite and Snow (1962) have quoted values of rate coefficients for several reactions. In particular (10) and (20) have the values 5×10^{-10} and 2×10^{-10} cm^3/sec respectively. Six (6) was found to be negligibly small and the reaction



is a two-body reaction with a rate coefficient of 5×10^{-13} cm^3/sec .

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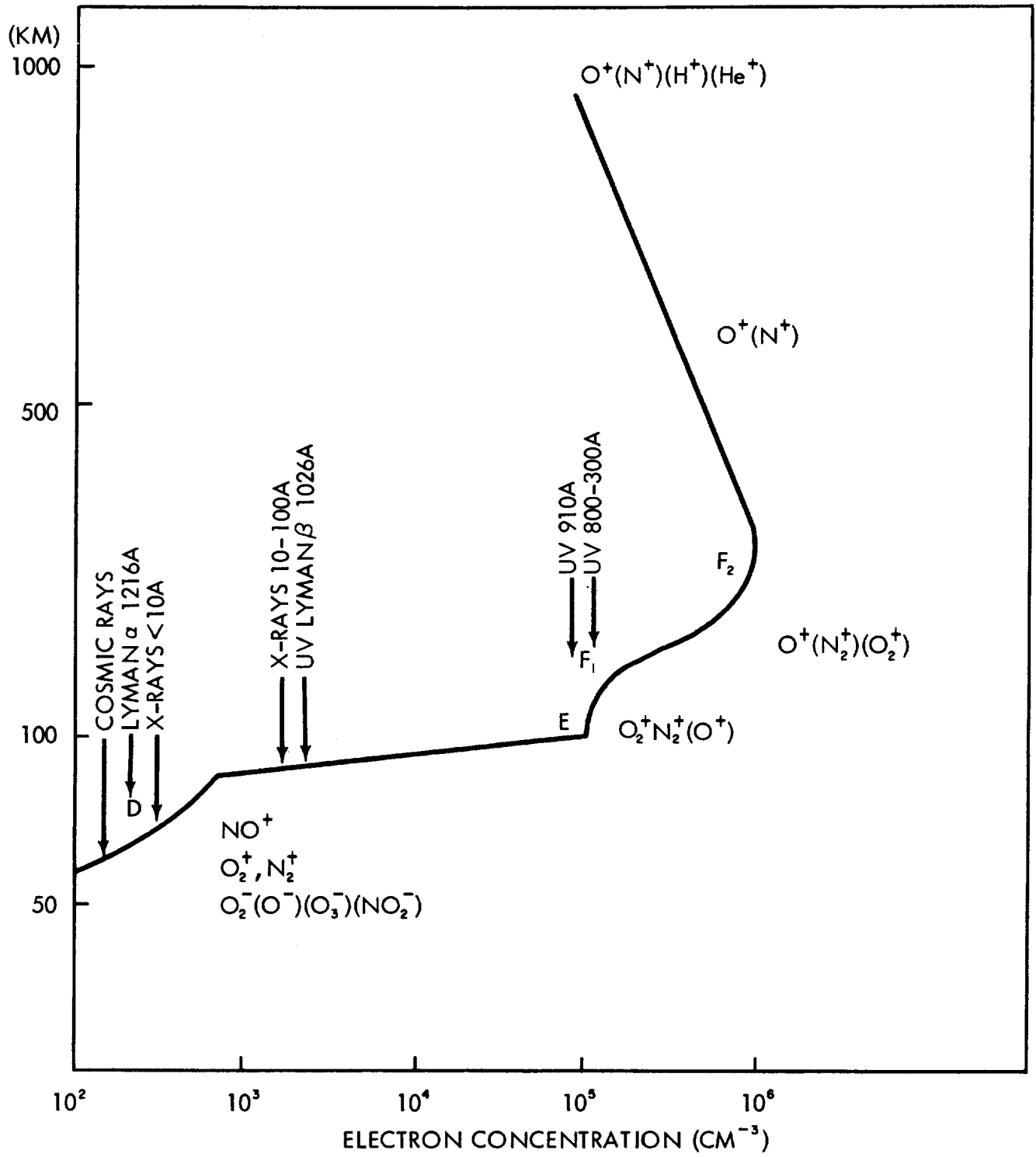
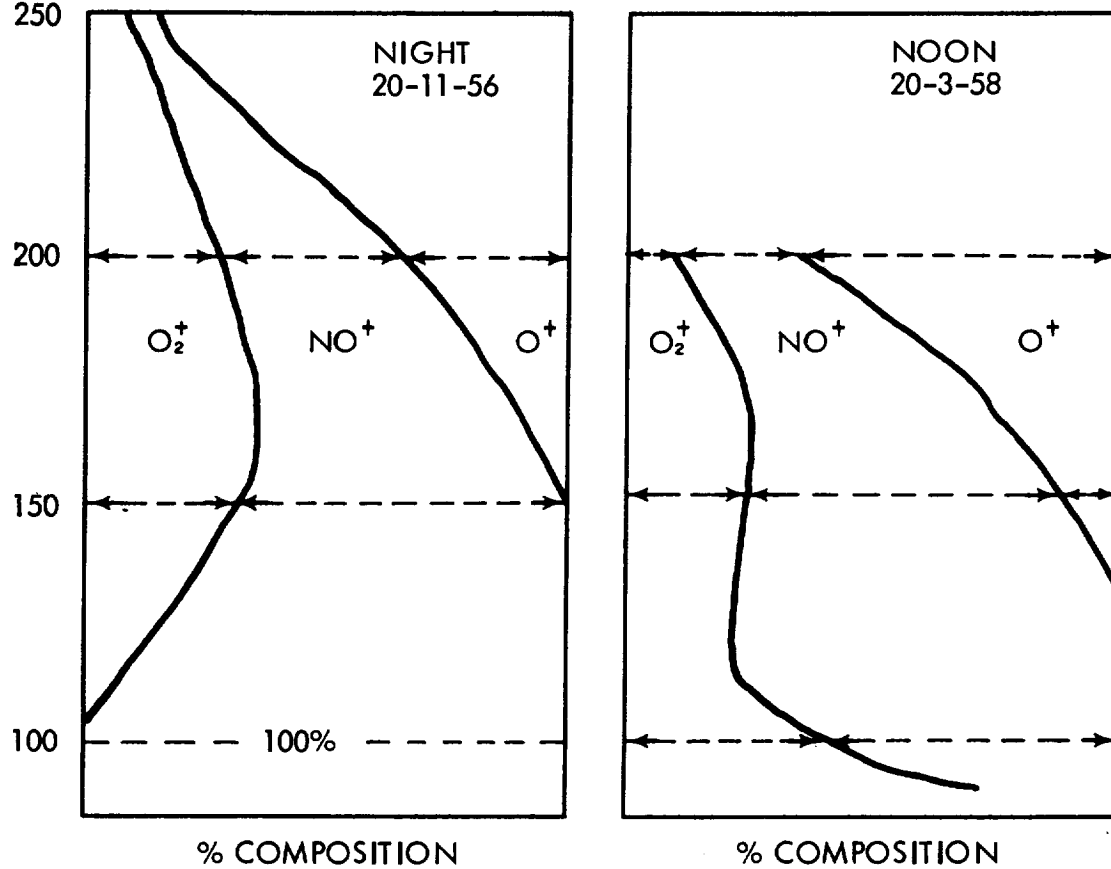


Figure 1

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WALLOPS ISLAND

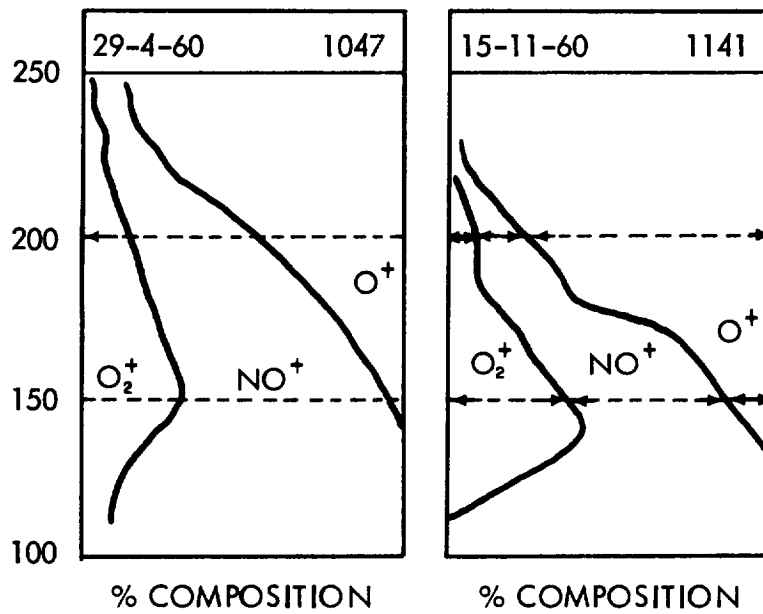


Figure 2